Removal of Ammonium and Organic Compounds by Ion Exchange and Adsorption

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Abstract

Adsorption using activated carbon and ion-exchange is used to remove a range of organic compounds and ammonia respectively from treated wastewaters. Such treatment may follow secondary biological treatment to reduce BOD. Organic nitrogen (e.g. proteins) is degraded to ammonia and residual organic compounds may also be present following secondary treatment. Residual organic compounds may be those which are recalcitrant and may include fatty acids, aromatic compounds, and detergents. Adsorption and ion exchange may offer an alternative to further biological treatment. Possible advantages include good response to shock loading, and low sensitivity to variations in temperature, pH, and anti-microbial activity. Three areas of investigation were undertaken and are described here; adsorption of organic acids onto activated carbon, the adsorption of aromatic compounds and proteins onto activated carbon and onto ion exchange resins, and the ion exchange removal of ammonium from an actual waste-water in the presence of organic compounds. Three cationic ion exchangers were studied: Clinoptilolite, Dowex 50w-x8 and, Purolite MN500. Three adsorbents were evaluated: two samples of activated carbon: Norit GAC 1240, and Aldrich activated carbon; and crushed glass (AFM). The results show that phenol, benzoic acid, methanoic, ethanoic, and propionic acid were successfully adsorbed on to the activated carbon. AFM was an ineffective adsorbent. It was also shown that successful ammonium removal by ion exchange in the presence of organic compounds was possible. In the presence of real wastewater, there were significant variations in the removal performance.

Introduction

As discharge limits for treated waste-water continue to become more stringent, tertiary treatment will become a requirement. The Council of the European Community [1] has set a guide level of 0.05mg/l and a maximum level of 0.5mg/l. New Zealand discharge standards vary from 0.22mg/l to 0.77mg/l [2]. In some cases biological methods may fail if the water contains antimicrobial chemicals. Some compounds may not be biodegradable and its also possible that the pH and temperature are outside suitable ranges for biological treatment. One possibility is the use of activated carbon to remove organic compounds and ion exchange to exchange ammonium with the less toxic sodium [3,4,5,6]. Applications range from the petrochemical sector to industries such as woolscouring. Ammoniacal nitrogen along with other organic compounds (some of which may be recalcitrant) also contributes to the overall BOD.

Three aspects are considered here:- (1) Removal of short chain fatty acids onto activated carbon by adsorption, (2) Adsorption of aromatic compounds and proteins onto activated carbon, AFM (crushed glass), and onto cationic exchange resins (3) The potential of ion exchangers for removal of ammonia and simultaneous sorption of organic compounds.

Experimental

Three ion exchangers were used in this study:- (1) Clinoptilolite[3,4], is a naturally occurring silica rich zeolite, which exhibits a high selectivity for ammonium; (2) Dowex 50w-x8 which is a strong acid, polystyrene based exchanger; (3) Purolite MN500 [7] is a hyper-crosslinked polymeric exchanger, exhibiting significant microporosity and macroporosity. Three adsorbents were also studies:- (1) Activated carbons: Norit GAC 1240, and Aldrich activated carbon (2) Crushed glass (AFM - Dryden Aqua). Determination of the equilibrium relationship for each system involved simple batchwise contact of the solid with the aqueous phase of preset solute loading. Upon equilibration the two phases were separated and the aqueous phase concentration with respect to ammonia was determined. The solid phase solute concentration was determined by mass balance.

All reagent chemicals were supplied by BDH and were of Analar grade. Whey protein isolate supplied by Fonterra Ltd. The woolscour water was secondary effluent supplied from Kaputone Wool Scour Ltd. Total organic acid content was determined by acid-base titration with NaOH, the concentrations of aromatic were determined by UV/vis spectrophotometry, protein content determined by means of assay kit (Sigma P5656), and ammonium determination using ion selective electrode (Hach).

ORGANIC CONTAMINANT	INITIAL CONCENTRATION
Methanoic acid	150mg/l
Ethanoic acid	150mg/l
Propionic acid	150mg/l
Phenol	235mg/l (2.5mmol/l)
Benzoic acid	305mg/l (2.5mmol/l)
Whey protein isolate	400mg/l
Ammonium (woolscour water)	576mg/l

The ion exchangers were preconditioned into the Na^+ form by step-wise contact with sodium chloride solution (10g/L) followed by water rinsing. For the adsorption uptake measurements the exchangers were preconditioned to H^+ form. This was to inhibit ion exchange from occurring during adsorption. In these cases the pH of the external solution was preset at pH 3.0, at pH 11.0, and unadjusted for pH.

The following isotherm models [8] were used to correlate the experimental results. (1) The Langmuir isotherm model:

$$Q_e = \frac{aC_e}{1+bC_e} \tag{1}$$

(2) The Freundlich isotherm model:

$$Q_e = x(C_e)^y \tag{2}$$

Q_e – Concentration of solute on solid phase at equilibrium (mg/g).
C_e – Concentration of solute in aqueous phase at equilibrium (mg/l).
a, b, x, and y – Constants applicable to a particular solute/solvent/solid system.

Results & Discussion

Figure 1 shows the adsorption of methanoic acid onto Norit activated carbon. An extrapolation of the Langmuir isotherm estimates a maximum capacity of 93mg/g reflecting significant removal capacity for methanoic acid. Each isotherm model showed a good fit. Figure 2 shows effective ethanoic acid adsorption and at a higher capacity than methanoic acid The Langmuir isotherm predicts a capacity of 78mg/g. Over the concentration range studied both isotherm models are satisfactory. Figure 3 shows analogous uptake by Aldrich activated carbon. Here the predicted maximum capacity (Figure 2) is 20mg/g. A comparison is shown in Figure 3

The adsorption of propionic acid onto Norit activated carbon (Figure 4) showed a maximum predicted capacity of 70mg/g with both models fitting the data. Figure 5 shows a comparison of each of the organic acids. For the Norit sample, comparison of the maximum uptake values for methanoic acid, ethanoic acid, and propionic acid respectively increase in that order. This could be explained by the lower polarity of the larger acids which reduces their affinity for the aqueous phase thus enhancing adsorption.

Figure 6 shows data for the uptake of phenol from water onto each of the adsorbents with the activated carbon showed the highest uptake. Purolite MN500 removed only a small amount of phenol which was surprising since its internal surface area would be comparable to that of activated carbon. Dowex 50w-x8 and the clinoptilolite showed insignificant removal of phenol. The adsorption of phenol onto activated carbon reduced with decreasing pH. This might be explained by formation of the anionic phenolate ion at high pH.

Figure 7 shows the experimental results for the uptake of benzoic acid from aqueous solution and to each of the adsorbents. The results are similar to those for phenol although at pH 11.0 the removal is significantly less than that at lower pH since the anionic form (benzoate) is not bas easily adsorbed as molecular benzoic acid.

The data for the adsorption of whey protein are shown in Figure 8, with activated carbon and the MN500 showing the highest uptake. In the cases of phenol and benzoic acid, activated carbon also showed the strongest uptake behaviour. The ion exchangers each show significant uptake of the protein which is highly pH dependent and is typical for proteins.

Figure 9 compares the uptake of ammonium ion onto clinoptilolite from synthetic NH_4Cl solutions with that from woolscour waste-water. In range 0–225mg/L (NH_4^+) the uptake from the synthetic solution is higher which may be attributed to other competitive ions present competing for sites and reducing ecapacity for ammonium ion. Above 225mg/l NH_4^+, uptake from the woolscour water is greater than that observed for the simulant.

Ammonium ion uptake on to Dowex 50w-x8 (Figure 10) from the wool-scour water was also substantially reduced compared with the pure solution. Significant competition from other cations would be a possible explanation. Another feature of the uptake from wool-scour waste water is that the isotherms differ significantly from that predicted by either the Langmuir or Freundlich models.

A third set of measurements, for ammonium ion uptake onto Purolite MN500, is shown in Figure 11. The linear equilibrium isotherm for the wool-scour water is observed. Earlier work [9] with synthetic solutions showed that the presence of only one organic species caused a slight enhancement in uptake at low NH_4^+ concentrations. Here the uptake from wool-scour waste water show enhancement only at higher concentrations. The shape of the isotherms differed significantly from that observed for uptake from pure ammonium chloride solutions. There was significant deviation from Langmuir type uptake, especially in the cases of the Dowex50w-x8 and the MN500. The result confirm the very significant differences which can occur in the behaviour of water treatment techniques when separation from actual effluents is required, compared with separation from laboratory prepared simulants

Conclusions

Short chain fatty acids can be successfully taken up from aqueous solutions onto activated carbon by adsorption. Over the concentration range studied here, equilibrium uptake capacity for the acids increased with increasing molecular weight, which suggests that the uptake of longer chain fatty acids would also be worthy of study. The two activated carbons studied showed different uptake capacities for ethanoic acid.

The ion exchangers Dowex 50w-x8, Purolite MN-500, and Clinoptilolite showed negligible adsorptive uptake capacity for either phenol or benzoic acid. In contrast, the activated carbons showed significant uptake of phenol and benzoic acid.

With the exception of AFM, all the material showed some uptake of whey protein, with the highest uptakes exhibited by the activated carbons and the MN500 resin. Uptake was dependent upon pH in all cases, with very strong dependence in the case of MN500 and in the case of clinoptilolite.

Ammonium ion was taken up from woolscour waste-water on to each of ion-exchangers. In the cases of Dowex50w-x8 and of MN500 the ammonium ion uptake equilibria from the wool-scour water deviated very significantly from Langmuir type behaviour, which contrasted with the uptake from pure solutions of ammonium chloride.

References

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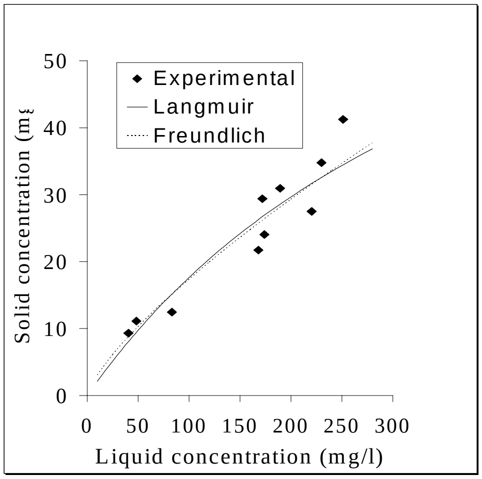

Fig 1 Adsorption of methanoic acid (Norit carbon)

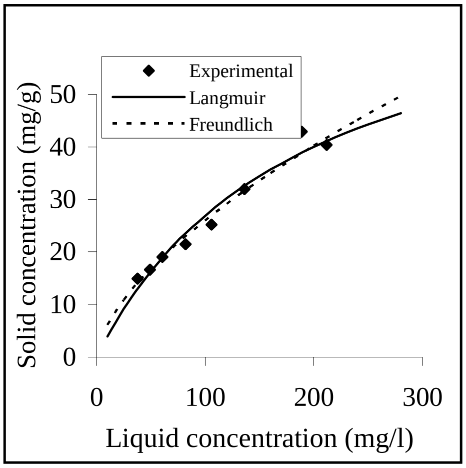

Fig 2 Adsorption of ethanoic acid (Norit carbon)

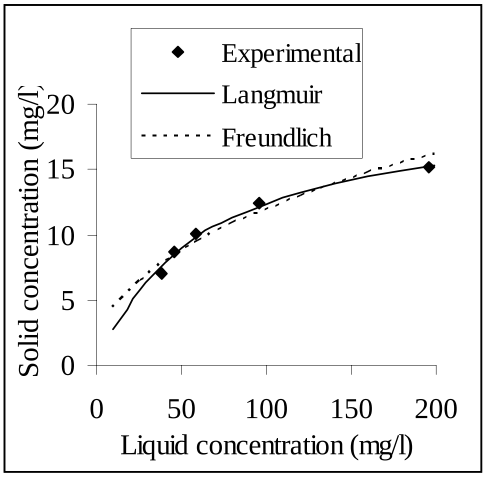

Fig 3 Adsorption of ethanoic acid (Aldrich carbon)

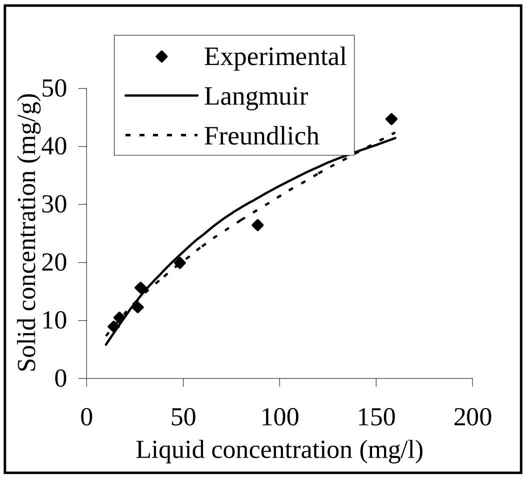

Fig 4 Adsorption of propionic acid (Norit carbon)

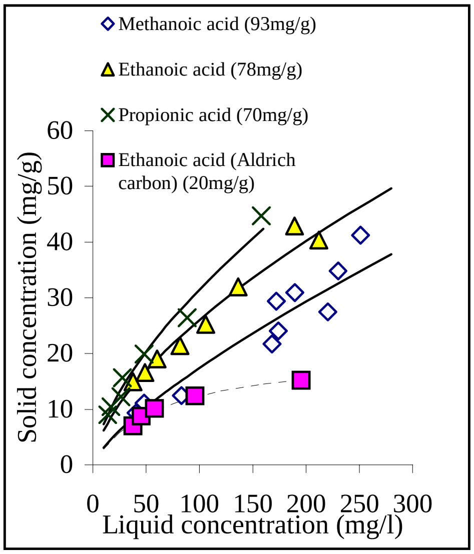

Fig 5 Comparison of adsorption onto carbons

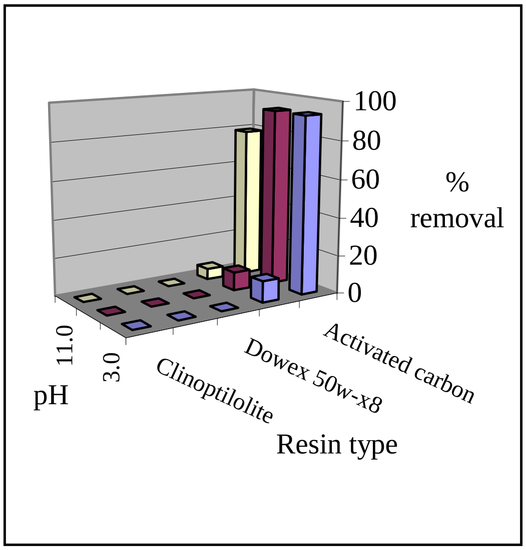

Fig 6 Batch adsorption of phenol

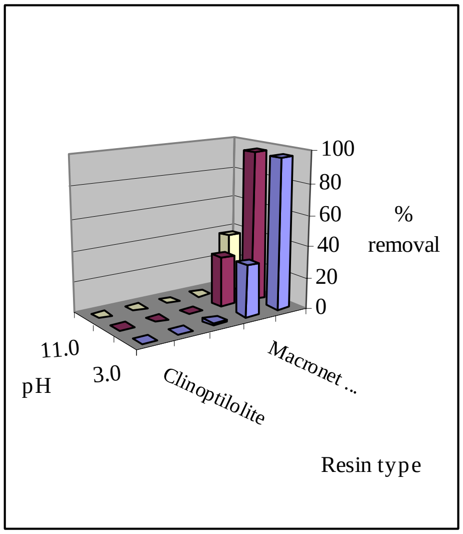

Figure 7 Batch adsorption of benzoic acid

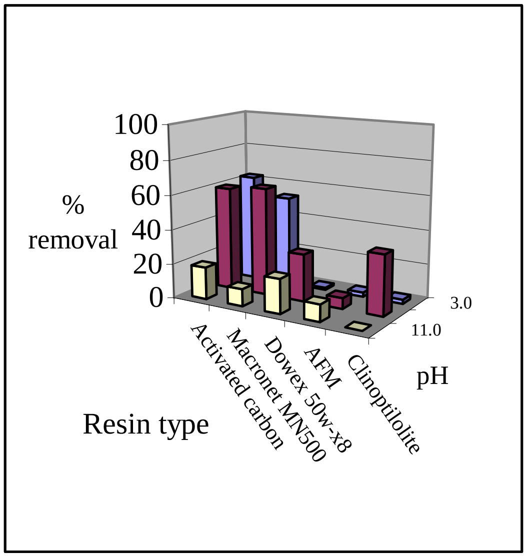

Figure 8 Batch adsorption of whey protein

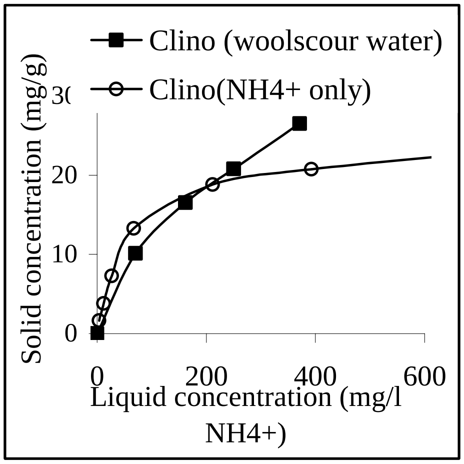

Fig 9 NH$_4^+$ uptake onto clino from wastewater

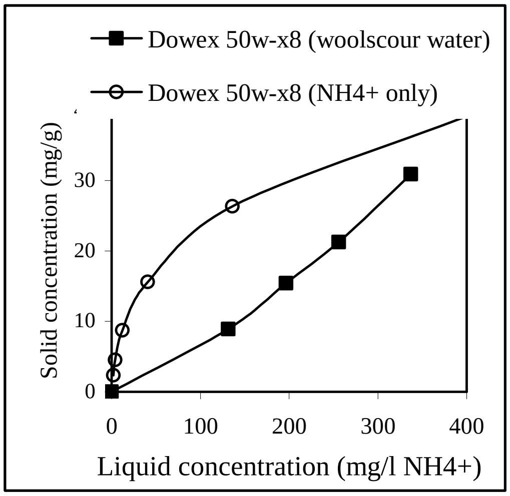

Fig 10 NH$_4^+$ uptake onto Dowex 50w-x8 from wastewater

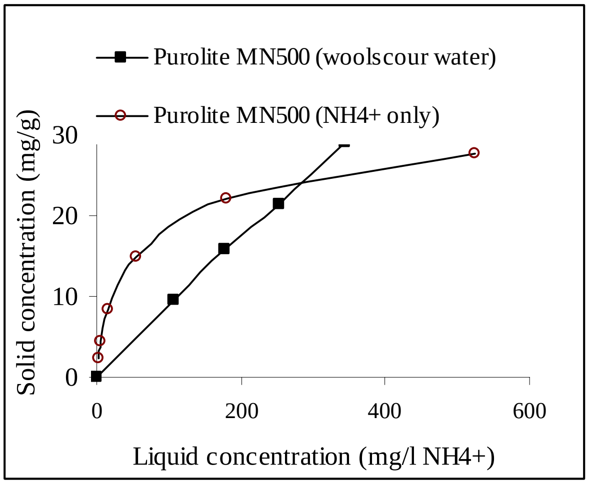

Fig 11 NH$_4^+$ uptake onto MN500 from wastewater